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Modified Born-Mayer equation for lattice energy calculation of ionic crystals

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The Born-Mayer equation in its generalised form without the use of the compressibility term has been further modified to yield better crystal energy data for 55 diatomic and 10 triatomic ionic crystals. Another empirical expression for lattice energy calculations, based upon the logarithmic repulsive term has also been suggested which yields yet better values agreeing closely with the recent experimental Born-Haber cyclic data. The one or two stage electron affinities of the negative atoms and the atomization energies of crystals tally closely with those reported in the literatures.

1. INTRODUCTION

Born-Mayer equation for the lattice energy in the generalised form

$$U_L = U_{ELEC}\left(1-\frac{\rho}{r_0}\right) \tag{1}$$

with ρ a constant equal to 0·345Å. U_{ELEC} is the Madelung term given by $NAe^2Z_1Z_2/r_0$ where the terms have their usual significance. From equation (1) we have

$$(U_{ELEC}-U_L)/U_{ELEC} = \frac{\rho}{r_0} \tag{2}$$

Thus a plot of $(U_{ELEC}-U_L)/U_{ELEC}$ against r_0^{-1} for various crystals should be a straight line passing through the origin with a slope of 0·345Å. Fig. 1 represents the plotted curve for alkali halide crystals together with the experimental points for which latest Born-Haber cyclic, U_L data, have been used (Woodcock 1974). It is found that the best statistical fit to the experimental points gives a straight line whose intercept at $r_0^{-1} = 0$ is not zero as predicted by equation (2) rather 0·085 and whose slope is 0·49282Å rather than 0·345Å. Thus Fig. 1 suggests that equation (1) should be modified to

$$U = U_{ELEC}\left(1\cdot085 - \frac{0\cdot49282}{r_0}\right) \tag{3}$$

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The above modified form of Born-Mayer equation simulates the combined effects of all weak interactions (such as Van der Waals, dipole-quadrupole term, etc.) existing between all unlike ion pairs. We thus expect that eq. (3) can yield better results than eq. (1). Yet this equation is based upon the exponential repulsive term which suffers from criticisms levied by different workers on

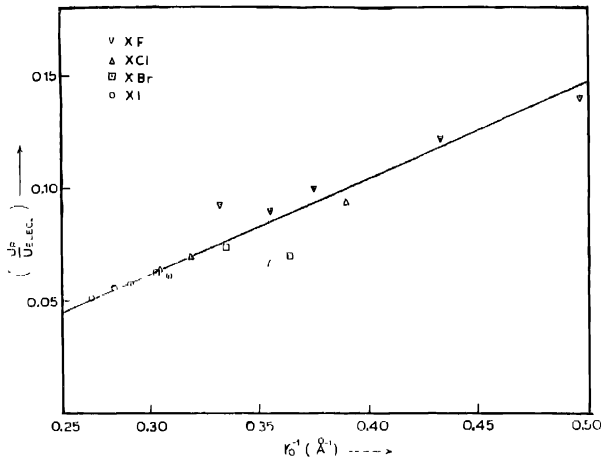

Fig. 1. Plot of $\frac{U_R}{U_{LEC}}$ against r_0^{-1} for alkali metal halide crystals.

different footings (Dobbs & Jones 1957, Woodcock 1974, Thakur 1976). Logarithmic form of lattice potential energy functions have been found to yield acceptable nature of potential energy and force curves (Thakur 1974, 1976). A general form of such an equation proposed recently (Thakur 1947, Thakur & Sinha 1977, Thakur, Sinha & Thakur 1977) is represented by

$$U_L = U_{ELE} \quad -\log_{10}(\alpha + \rho r_0^{-2}) \tag{4}$$

where α and ρ are parameters. Equation (4) suggests that a plot of $\log_{10}(U_{ELEC} - U_L/U_{ELEC})$ against r_0^{-2} for the ionic crystals should be a straight line having slope ρ and intercept α at $r_0^{-2} = 0$. This curve has been plotted in Fig. for alkali halides. For this curve we get $\alpha = 1{\cdot}015$ and $\rho = 1{\cdot}60416$ Å^2.

The ratio of repulsive term to the electrostatic term according to eqs. (1), (3) and (4), respectively, are

$$\frac{U_R}{U_{ELEC}} \qquad \ldots (5)$$

$$\frac{U_R}{U_{ELEC}} \quad (0{\cdot}49282 - 0{\cdot}085 r_0) r_0^{-1}, \tag{6}$$

and

$$\frac{U_R}{U_{ELEC}} = \log_{10}(a + p r_0^{-2}) \tag{7}$$

In Fig. 3, U_R/U_{ELEC} against r_0 according to eqs (5), (6) and (7) together with the experimental points for alkali halides have been plotted

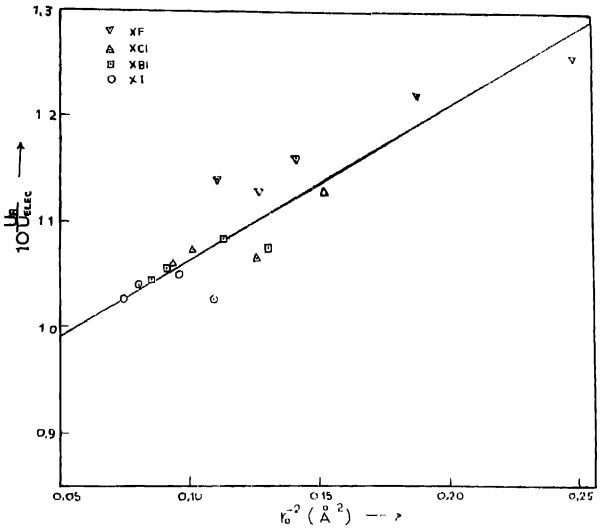

Fig. 2 Plot of $\frac{U_R}{U_{ELEC}}$ against r_0^{-2}(Å^{-2}) for alkali metal halide crystals

It is found that the curves due to eqs (6) and (7) are similar upto a considerable range and experimental points are also close to these curves whereas the curve due to eq (5) is much away from the experimental points. This curve shows the superiority of eq. (4) over eq (1).

2 Calculation and Results

Lattice energy

Tables 1, 2 and 3 list the r_0 values and the computed values of the lattice energies for 55 diatomic ionic crystals from eqs (1), (3) and (4) together with the available experimental (cyclic) data compiled by Woodcock (1974), Waddington (1959), Thakur (1974) Thakur, Sinha & Thakur (1977) and Pandey (1970) In

table 4 lattice energies of triatomic alkali metal oxides and sulphides have been calculated

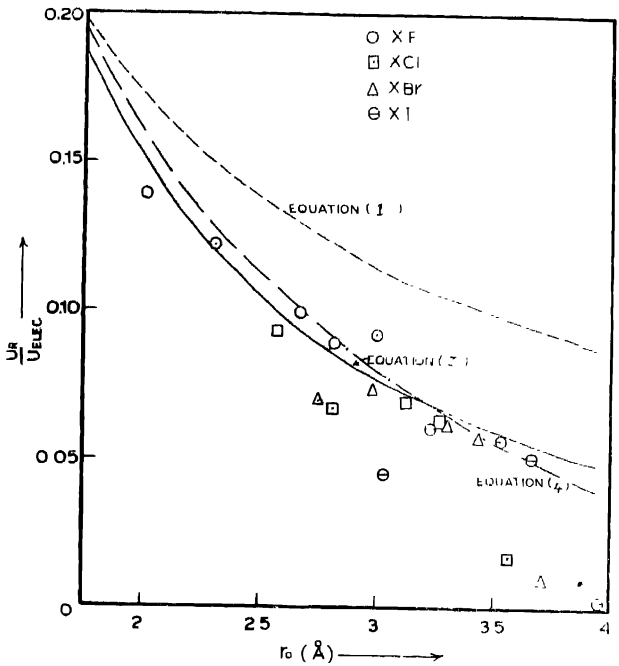

Fig 3 Plot of $\frac{U_R}{U_{ELEC}}$ against r_0(Å) for alkali metal halide crystals

Table 1 shows that the average percentage error for alkali halide crystals is maximum according to Born-Mayer equation (1) and minimum according to equation (4) whereas the modified Born-Mayer eq. (3) yields values in between the two Table 2 shows the same pattern. The agreement between the experimental (cyclic) and calculated values are satisfactory considering the uncertainty involved in measurements of the r_0 and the enthalpy terms. Mayer & Maltbie (1932) have improved upon the lattice energies of chalcide crystals by including the Van der Waals term and the zero-point energy. It can be seen that eq. (4) values are very close to the cyclic data and eq. (3) gives better values than the so-called Mayer & Maltbie's (1932) refined values. Eq. (1) yields only marginal agreement with the experimental data.

Table 1. Values of interionic distance r_0(Å) and the lattice energy U_L(kJ mol^{-1}) of alkali halide crystals

Crystals	r_0 Wells (1962)	U_L Cyclic*	Calc. Eq. (3)	Calc. Eq. (4)	Calc. Eq. (5)
LiF	2·009	1039·8	1013·6	1035·2	1000
NaF	2·307	922·8	916·0	925·7	894
KF	2·664	819·9	819·3	825·0	792
RbF	2·815	784·8	783·9	787·9	756
CsF	3·005	732·5	743·3	745·3	714
LiCl	2·566	857·6	843·9	850·7	818
NaCl	2·814	801·1	781·1	788·2	756
KCl	3·139	719·1	716·9	717·7	687
RbCl	3·285	691·7	690·2	689·7	661
CsCl	3·560	675·5	650·1	647·6	621
LiBr	2·747	821·6	799·5	801·2	772
NaBr	2·981	753·8	748·2	750·4	719
KBr	3·293	690·6	688·8	688·2	659
RbBr	3·431	665·9	665·9	663·4	635
CsBr	3·713	652·5	627·3	623·5	598
LiI	3·025	765·9	739·2	741·0	710
NaI	3·231	705·3	700·0	699·8	670
KI	3·526	649·6	650·1	647·6	620
RbI	3·663	628·7	629·3	625·8	600
CsI	3·950	618·2	594·6	589·3	565
Average error (%)			1·5	1·4	5·1

* Woodcock (1974)

Table 3 lists U_L values for ammonium and heavy metal halides. The agreement of ammonium chloride through iodide and thallium halide crystals with the experimental thermochemical cyclic data is excellent. There is poor agreement for the rest of the halides. The difference in ammonium fluoride is attributed to the hydrogen bonding in the crystal (Waddington 1959). The deviations from the cyclic data in the case of Cu, Ag and Tl halides increase in the following order $F < Cl < Br < I$ and $Tl^{I} < Ag^{I} < Cu^{I}$. Morris & Ahrens (1956) have suggested this anomaly as due to increasing polarizability and decreasing ionic radii of the ions which make the molecules deviate from polarity.

Table 2 Values of interionic distance r_0(Å) and the lattice energy, U_L (kJ mol^{-1}) of alkaline-earth chalcide crystals

Crystal	(A) (*a*)	Cyclic (*a*)	Calc Eq (3)	Calc Eq (4)	Calc Eq (1)	Mayer & Mattlue (1932)
BeO	1 649	4540	4343	4390	4369	3929
MgO	2 105	3899	3921	3968	3853	3477
CaO	2 405	4512	3550	3584	3455	3205
SrO	2 580	3332	3361	3388	3257	3042
BaO	2 770	3289	3177	3194	3066	
BeS	2 105	3910	3676	3720	3612	3347
MgS	2 602	3348	3339	3364	3234	3084
CaS	2 846	3197	3108	3123	2995	2870
SrS	3 010	3012	2969	2977	2853	2707
BaS	3 194	2841	2827	2828	2709	
BeSe	2 225		3520	3569	3453	
MgSe	2 731	3339	3213	3233	3103	
CaSe	2 962	3038	3008	3018	2892	
SrSe	3 122	2900	2881	2884	2764	
BaSe	3 302	2761	2749	2746	2631	
BeTe	2 436		3295	3326	3204	
MgTe	2 770	3148	2981	3000	2879	
CaTe	3 179	2841	2838	2839	2720	
SrTe	3 331	2791	2729	2725	2611	
BaTe	3 500	2632	2617	2608	2498	
range error (%)			1 96	1·88	1 91	3·25

akur (1974) Thakur & Pandey (1975)

Table 3 Values of interionic distance r_0(Å) and lattice energy U_L (kJ mol^{-1}) of ammonium and heavy metal halide crystals

Crystal	(A) (*a*)	Cyclic (*b*)	Calc Eq (3)	Calc Eq (4)	Calc. Eq (1)
NHF	2·63	738·1	777 0	782 6	752 1
NHCl	3 34	681 2	686·5	685·5	656 7
NHBr	3·51	649 4	658·3	655·8	630·2
NHI	3 78	613 8	617·7	613 6	588·0
TlF	2·59	828 4	837·8	844 3	811 6
TlCl	3 33	698 7	688 3	687 3	658·4
TlBr	3 44	689 2	669·6	667·7	639 7
TlI	3·62	673 8	641 1	637 9	611 3
CuF	1 85		1005 0	1018 3	999 7
CuCl	2·35	928·1	846 7	855 3	852 3
CuBr	2 46	903·7	817 4	823·9	794 4
CuI	2·62	892 2	778 2	783·9	753 1
AgF	2 46	910 9	872 1	880 1	847 6
AgCl	2 77	849 1	794 1	798·6	766 5
AgBr	2·89	824 3	767 3	770·6	738 9
AgI	2·80	832·6	739·0	742 9	712 8

(*a*) Seitz (1940) and Sanderson (1977)
(*b*) Waddington (1959) and Pandey (1969).

Table 4 presents the lattice energies of alkali metal chalcide crystals Waddington (1959) has tabulated calculated values from the work of Sherman, West, and Morris wherein the original references have been mentioned. The present values are in agreement with the previous ones

Table 4. Input data and the lattice energy of alkali metal chalcide crystals

Crystals	A (Madelung constant)	r_0(A) (a)	U_L(kJ mole^{-1}) Calc Eq (3)	Calc Eq (4)	Calc Eq (1)
Li_2O	5·04	2·00	2933	2969	2894
Na_2O	5·04	2·41	2555	2570	2487
K_2O	5·04	2·79	2277	2289	2197
Rb_2O	5·04	2·92	2195	2203	2112
Cs_2O	4·38	2·86	1940	1949	1869
Li_2S	5·04	2·48	2500	2522	2428
Na_2S	5·04	2·82	2258	2269	2177
K_2S	5·04	3·20	2035	2035	1950
Rb_2S	5·04	3·32	1973	1970	1888
Cs_2S	5·04	3·48	1896	1890	1811

(a) Sanderson (1977)

Electron Affinity

The electron affinity of an atom X is given by the equation

$$E(X) = U_L + nRT - \Delta H_f^0 MX(c) - \Delta H_f^0 M^{n+}(g) - \frac{D}{2} X_2 \qquad (7)$$

where $\Delta H_f^0 MX(c)$ and $\Delta H_f^0 M^{n+}(g)$ are the standard heats of formation of the crystalline compound and the gaseous positive ion respectively, and $D(X_2)$ the molar dissociation energy of halogen or chalcogen. The term nRT is added as PV correction to bring the ionic species from 0°K to 298°K and this for a diatomic crystal is 5 kJ mol^{-1} and for a triatomic crystal 7 kJ mol^{-1}. All these terms have been compiled from Pritchard (1953). Parker *et al* (1971) and Wagman *et al* (1965) and have been presented in Tables 5 and 6. The computed values of $E(X)$ are presented in Tables 7 and 8 using U_L values computed from eqs. (3) and (4), respectively. These compare satisfactorily with the recent experimental values of Berry & Reimen (1963), Franklin & Harland (1974), Cubicciotti (1961), Huggins & Sakamoto (1957). Morris (1957) and Cantor (1973)

Table 5. Input data of alkali halide crystals in kJ mol^{-1}

Crystals	$\Delta H_f^0 MX(c)$	$\Delta H_f^0 M^{n+}(g)$	$\frac{D}{2} X_2$	I
	(*a*)	(*a*)	(*a*)	(*b*)
LiF	612	682	78 3	520·1
NaF	569	611	78.3	195·4
KF	563	515	78·3	418·4
RbF	549	495	78 3	402·9
CsF	531	461	78·3	373·6
LiCl	409	682	120·9	520·1
NaCl	411	611	120·9	495·4
KCl	436	515	120·9	418·4
RbCl	431	495	120·9	402·9
CsCl	433	461	120·9	373 6
LiBr	350	682	112·2	520·1
NaBr	360	611	112 2	495·4
KBr	392	515	112 2	418·4
RbBr	389	495	112 2	402 9
CsBr	395	461	112 2	373 6
LiI	271	682	107·0	520·1
NaI	288	611	107 0	495 4
KI	328	515	107·0	418 4
RbI	328	495	107·0	402·9
CsI	337	461	107·0	373 6

(*a*) Pritchard (1953), Parker *et al* (1971), Wagman *et al* (1965)
(*b*) Greenwood (1968)

Table 6. Input data of alkaline-earth chalcogenide crystals in kJ mole^{-1}.

Crystals	$\Delta H_f^0 MX(c)$	$\Delta H_f^0 M(g)$	$\frac{D}{2} X_2$	$\sum_1^n In$
	(*a*)	(*a*)	(*a*)	(*b*)
BeO	610	2993	249 4	2656
MgO	602	2348	,,	2188
CaO	635	1926	,,	1735
SrO	592	1791	,,	1613
BaO	554	1660	,,	1467
BeS	234	2993	278·7	2656
MgS	347	2348	,,	2188
CaS	482	1926	,,	1735
SrS	453	1791	,,	1613
BaS	460	1660	,,	1467
BeSe		2993	205 9	2656
MgSe	—	2348	,,	2188
CaSe	368	1926	,,	1735
SrSe	386	1791	,,	1613
BaSe	372	1660	,,	1467
BeTe	—	2993	190·4	2656
MgTe	209	2348	,,	2188
CaTe	—	1926	,,	1735
SrTe	—	1791	,,	1613
BaTe		1660		1467

(*a*) Pritchard (1953), Parker *et al* (1971), Wagmann *et al* (1965)
(*b*) Greenwood (1968).

Table 7. Values of electron affinity of atoms and atomization energy of crystals at 298°K (in kJ mol^{-1}).

Crystals	U_L+nRT Eq. (3)	$H_f^0X^{n-}$ (Calc.)	$H_f^0X^{n-}$ Mean	$E(X)$ (Calc.)	$E(X)$ (Exptl.) (*a*)	H_a (Calc.)	H_a (Exptl.) (*b*)
LiF	1019	- 276				831	853
NaF	921	- 259				761	761
KF	824	−254	−257·4	335·7	332 7	742	736
RbF	789	−255			−332·9	722	710
CsF	748	−244			−332·6	710	688
LiCl	849	-242					
NaCl	789	−233				684	691
KCl	722	−229	−234 7	- 355·6	−348 6	649	641
RbCl	695	- 231			- 348·3	659	647
CsCl	655	-238			357·7	648	634
						637	633
LiBr	805	-228					
NaBr	753	-218				616	623
KBr	694	213	−219·2	−331·4	321·5	589	580
RbBr	670	- 214			324·2	607	580
CsBr	632	−224			−336 7	598	583
						590	584
LiI	744	209					
NaI	705	−191				527	538
KI	655	−188	195 6	−302·6	- 295·5	512	503
RbI	634	−189			−296 2	539	523
CsI	600	−198			−307·6	534	517
						529	522
BeO	4348	745					
MgO	3926	976				1008	1176
CaO	3555	994	933 2	683 8	678 ± 63	1054	1041
SrO	3366	983			631	1136	1062
BaO	3182	968			623	1069	1003
						1031	983
BeS	3681	454					
MgS	3344	649				654	840
CaS	3113	705	650 0	371 1	414 ± 63	786	806
SrS	2974	730				1007	917
BaS	2832	712				989	894
						993	898
BeSe	3534	-					
MgSe	3218	-				367	
CaSe	3013	719	716·7	511 0	489 ± 63	519	626
SrSe	2886	709				707	703
BaSe	2754	722				762	649
						776	690
BeTe	3300	-					
MgTe	2989	-				—	
CaTe	2843	432	432 0	241 6	406 ± 84	-	—
SrTe	2734						
BaTe	2622						

(*a*) Berry & Reimann (1963), Franklin & Hauland (1974), Cubicciotti (1961).
(*b*) Sanderson (1977).

Atomization Energy

The atomization energy ΔH_a of a crystal can be derived from

$$\Delta H_a = U_L+nRT-\sum_1^n I-E(X) \qquad (9)$$

Table 8. Values of electron affinity of atoms and atomization energy of crystals at 298°K (in kJ mol^{-1}).

Crystals	$U_L + nRT$ Eq. (4)	$\Delta H_f^\circ X^{n-}$ (Calc.)	Mean	$E(X)$ (Calc.)	$E(X)$ (Exptl.) (*a*)	ΔH_a (Calc.)	ΔH_a (Extpl.) (*b*)
LiF	1040	−254				847	853
NaF	931	−249			−332 7	762	761
KF	830	−248	−248 8	−327 1	−332·9	739	736
RbF	793	−251			−332 6	717	710
CsF	750	−242				704	688
LiCl	856	−235				690	691
NaCl	793	229			−348·6	651	641
KCl	723	−228	−232 8	−353·7	−348·3	658	647
RbCl	695	−231			−357 7	646	634
CsCl	653	−241				633	633
LiBr	809	−223				620	623
NaBr	755	216			−324 5	591	580
KBr	693	−214	−219·2	−331 4	−324 2	606	580
RbBr	668	−216			−336 7	597	583
CsBr	629	−227				587	584
LiI	746	−207				530	538
NaI	705	−194			−295 5	514	503
KI	653	−190	197·4	304·4	296 2	539	523
RbI	631	−192			307 6	533	517
CsI	594	−204				525	522
BeO	4395	792				1021	1176
MgO	3973	1023			678 ± 63	1067	1041
CaO	3589	1028	967·6	718 2	631	1136	1062
SrO	3393	1010			623	1061	1003
BaO	3199	985				1013	983
BeS	3725	498				679	840
MgS	3360	674				791	806
CaS	3128	720	668 6	389 9	414 ± 63	1003	917
SrS	2982	738				979	894
BaS	2833	713				976	898
BeSe	3574					404	
MgSe	3238					536	626
CaSe	3023	729	720 0	514 2	489 ± 63	774	703
SrSe	2889	712				761	649
BaSe	2751	719				770	690
BeTe	3331						
MgTe	3005	148					
CaTe	2844	-	148 0	258 0	406 ± 84		
SrTe	2730	-					
BaTe	2613	-					

(*a*) Berry & Reimann (1963), Franklin & Harland (1974), Cubiccotti (1961), Canton (1973) Morris (1957).
(*b*) Sanderson (1977)

where $\sum_{1}^{n} I$ is the sum of ionization potentials of the metal atom to produce positive ion and these have been used from Greenwood (1968)

Tables 7 and 8 show that there is a good agreement between the calculated and the experimental values.

3. Discussion

Thus we conclude that the calculated values of the lattice energy, atomization energy and electron affinity obtained from the modified Born-Mayer equation and logarithmic form of equation compare excellently well with the available data. Generally, the computation of the lattice energy requires among others a knowledge of the compressibility data at 0°K which is difficult to measure correctly. But eqs (1), (3) and (4) have the property such that they can fit energy data of a crystal even without the compressibility term. Eq. (4) yields even better results than the Born-Mayer and modified Born-Mayer equations. Fig. 3 also shows the superiority of eq. (4) over the Born-Mayer equation. Thus the present calculations establish the applicability and usefulness of the new lattice energy equations based upon either an exponential or a logarithmic form of repulsive term (Thakur 1976b) to calculate the crystal energies.

References

Berry R. S. & Reeman C. W. 1963 *J. Chem. Phys.* **38**, 1544

Cantor S. 1973 *J. Chem. Phys.* **59**, 5189

Cubicciotti D. 1961 *J. Chem. Phys.* **34**, 2189

Dobbs E. R. & Jones G. C. 1957 *Rep. Prog. Phys.* **20**, 516, 522

Franklin J. L. & Haland F. W. 1974 *Ann. Rev. Phys. Chem.* **24**, 485

Greenwood N. N. 1968 *Ionic crystals lattice defects and non-stoichiometry* (Butterworths, London) p. 182

Huggins M. L. & Sakamoto Y. 1957 *J. Phys. Soc. Japan* **12**, 241

Mayer J. E. & Multhie M. 1932 *Z. Phys.* **75**, 748.

Morris D. F. C. 1957 *Proc. R. Soc.* **A242**, 126

Morris D. F. C. & Ahrens L. H. 1956 *J. Inorg. Nucl. Chem.* **3**, 263

Pandey J. D. 1969 *J. Phys. Soc. Japan* **26**, 579.

Pandey J. D. 1970 *Z. Phys. Chem. Leipzig* **243**, 221

Parker V. B., Wagman D. D. & Evans W. H. 1971 *Technical Note* 270-6 (N. B. S. Washington D.C.)

Pritchard H. O. 1953 *Chem. Phys.* **52**, 529.

Sanderson R. T. 1977 *Chemical Bonds and Bond Energy* (Academic Press, London)

Seitz F. 1940 *The Modern Theory of Solids* (McGraw-Hill, New York), p. 654

Thakur K. P. 1974 *Ind. J. Chem.* **12**, 376

Thakur K. P. 1976a *J. Inorg. Nucl. Chem.* **38**, 1433

Thakur K. P. 1976b *Aust. J. Phys.* **29**, 39.

Thakur K. P. & Pandey J. D. 1975 *J. Inorg. Nucl. Chem.* **37**, 645

Thakur L. & Sinha A. K. 1977 *Ind. J. Pure Appl. Phys.* **15**, 115.

Thakur L., Sinha A. K. & Thakur K. P. 1977 *Phys. Rev. B.* (in press); also *Proc. 26th IUPAC Congress, Tokyo, Japan*, 1977 p. 620

Waddington T. C. 1959 *Advances in Inorganic and Radiochemistry* **1**, 190.

Wagman D. D., Evans W. H., Halow I., Parker V. B., Bailey S. M. & Schumm R. H. 1965 *Technical Note* 270-1, (N.B.S. Washington, D.C.).

Wells A. F. 1962 *Structural Inorganic Chemistry*, Oxford, 3rd edn., p. 357.

Woodcock L. V. 1974 *J. C. S. Faraday II*, **70**, 1405.